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CHEMISTRY

FURFURYLIDENE- AND BENZYLIDENE-PHENOL SYSTEMS AND THEIR FUSIBILITY DIAGRAMS

By V. V. Čelincev, Corresponding Member of the Academy

It being very important to obtain purely-organic complexes with a view to a further elucidation of the types and structures of oxonium compounds, we proceeded to determine the fusibility curves of furfurylidene compounds with diatomic phenols.

Independently of our work G. M. Bennett and R. L. Wain (1) did something of the kind with regard to complexes of a somewhat different nature, namely with regard to oxido-phenol complexes of cyclic oxides of the hydrofurane and the hydro-pyrane series.

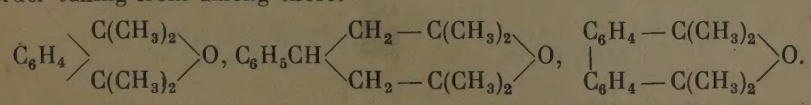
From our thermochemical determinations (2) we knew that ketone compounds (their carbonyl groups) possesses much more strongly pronounced higher oxonium valencies than those possessed by oxides or ethers. This was the reason why we chose ketone compounds for our experiments, taking them from the series of furfurylidene and benzylidene derivatives. As to the furane nucleus itself, its oxygen, in the presence of double bonds in the neighbouring carbon atoms, does not display, as shown by our previous investigations (3), any perceptible higher valencies, and what we counted on was thus only the carbonyl groups of the above compounds.

For a comparison of the relative strength of the higher valencies in carbonyl atoms and in ether or oxide oxygen atoms we give below the thermal effects obtained by the action of either group of compounds on individual magnesium-organic alcoholates:

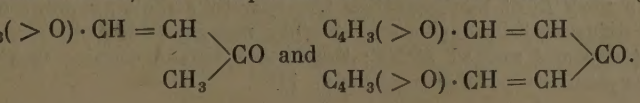
$$\text{I} > \text{C}:\text{O} \lessdot \quad -Q = 14.4 \text{ Cal},$$

$$\text{II} \gtrless \text{C} > \text{O} \lessdot \quad -Q = 4.8 \text{ Cal}.$$

G. M. Bennett and R. L. Wain had made use of compounds of the II order taking from among those:



We took, however, for our determinations furfurylidene acetone, and difurfurylidene acetone, i. e. compounds of the I order with ketone groups:

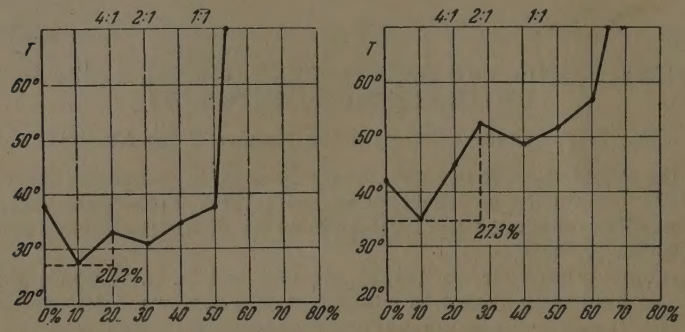


Furthermore, parallel to these, we took for verification and comparison also benzylidene acetone and dibenzylidene acetone:

$$C_6H_5 \cdot CH = CH \diagdown \atop CH_3 \diagup CO \text{ and } \begin{matrix} C_6H_5 \cdot CH = CH \diagdown \\ C_6H_5 \cdot CH = CH \diagup \end{matrix} CO.$$

All the determinations made by the writer in collaboration with V. I. and G. I. Kuznecov, have been divided into two series: the first series com-

Fig. 1. WEIGHT QUANTITIES DIAGRAM
(Weight percentages of phenols plotted on the axis of abscissae)

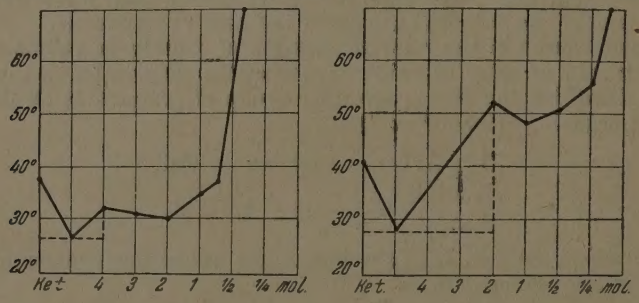


Monofurfurylidene acetone+ +hydroquinone

Monobenzylidene acetone+ +pyrocatechin

prising the monofurfurylidene-acetone and the monobenzylidene-acetone systems and the second comprising the difurfurylidene-acetone and the dibenzylidene-acetone systems.

Fig. 2. MOLECULAR RATIO DIAGRAM
(Number of ketone moles per one phenol mole plotted on the axis of abscissae)



Monofurfurylidene acetone+ +hydroquinone

Monobenzylidene acetone+ +pyrocatechin

The monofurfurylidene acetone was used as a nearly colourless preparation, melting point 39°; the monobenzylidene acetone was a preparation having a very faint lemon-yellow tinge, with a melting point of 42°.

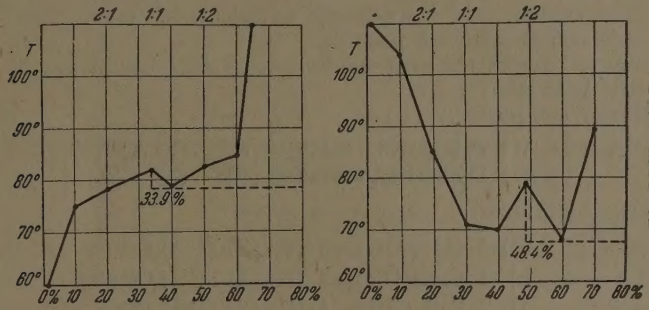
The difurfurylidene acetone, freshly recrystallized, had a faint pale-yellow tinge and melted at 58°; the dibenzylidene acetone was a greenish-yellow crystalline powder melting at 112°.

The phenols had their usual melting points: pyrocatechin, 105°; resorcine, 110°; hydroquinone, 171°.

The experiments with monofurfurylidene acetone and the parallel experiments with monobenzylidene acetone gave the following results.

With pyrocatechin an unmistakable rise was obtained in the 20—30% phenol+80—70% ketone range with a melting point of 51°.

Fig. 3. WEIGHT QUANTITIES DIAGRAM
(Weight percentages of phenols plotted on the axis of abscissae)



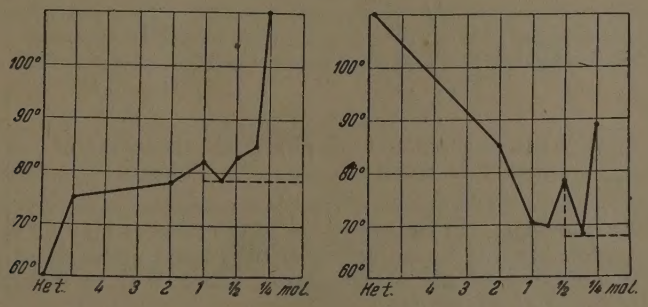
Difurfurylidene acetone+ +hydroquinone

Dibenzylidene acetone+ +pyrocatechin

With resorcine an analogous rise was obtained in the 20—30% phenol+80—70% ketone range, melting point 39°; the melts obtained in 50—60% phenol+50—40% ketone range do not crystallize readily and have no clearly defined melting points.

Hydroquinone gave a rise throughout, with a well-defined maximum in the 20—30% phenol+80—70% ketone range, melting point about 81°.

Fig. 4. MOLECULAR RATIO DIAGRAM
(Number of ketone moles per one phenol mole plotted on the axis of abscissae)



Difurfurylidene acetone+ +hydroquinone

Dibenzylidene acetone+ +phyrocatechin

The diagrams given on page 348 show the typical fusibility curves of these substances.

Identical experiments carried out with difurfurylidene acetone and dibenzylidene acetone respectively gave the following results.

Pyrocatechin gave an unmistakable rise in the 50% phenol+50% ketone range.

Resorcine yielded two maxima, one approximately in the 20% phenol+ +80% ketone range, and another in the 30—40% phenol+70—60% ketone range.

Hydroquinone gave a rise in the 30% phenol+70% ketone range.

It is interesting to note that just at the points stated above there occurred the characteristic change of colour in the products.

The diagrams given on page 349 show the typical fusibilily curves of the above substances.

The data obtained justify the conclusion that ketones, i. e. in our case furfurylidene acetone and benzylidene acetone (both mono- and di-) form unmistakable complexes with phenols.

We claim to have established the following new complexes of the compounds dealt with above.

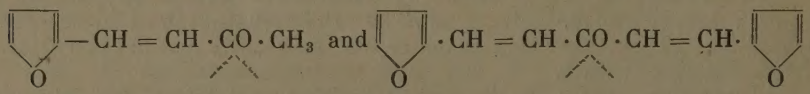
Monolidene complexes:

a′) 1 $C_6H_4(OH)_2 \cdot 4R \cdot CH : CH_2 \cdot CO \cdot CH_3$;
a″) 1 $C_6H_4(OH)_2 \cdot 2R \cdot CH : CH \cdot CO \cdot CH_3$.

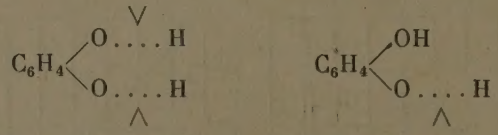
Di-lidene complexes:

a″) 1 $C_6H_4(OH)_2 \cdot 2\ (R \cdot CH : CH)_2CO$;
b) 1 $C_6H_4(OH)_2 \cdot 1\ (R \cdot CH : CH)_2CO$;
c) 2 $C_6H_4(OH)_2 \cdot 1\ (R \cdot CH : CH)_2CO$.

According to the theory of oxonium forms developed by us the structure of the complexes obtained may be accounted for by the supposition that the oxygen of the carbonyl group of ketones passes into the tetravalent state:



As to the oxygen atom of the furane rings, it does not, as shown by our calorimetric determinations, display any higher valencies. The phenol molecules combine with these higher valencies after having been previously split up, which occurs, in the first two cases a″), b), according to the formula:



a) When the amount of phenol is small

b) With an excess of phenol

In c) case, where the formation of complexes is accompanied by the appearance of bright colours, an isomerization of the ketones may be supposed to take place, probably due to the action of the second molecule of phenol on the ketone molecules of the b) complexes, which will be investigated by us in fuller detail at a later date.

V. I. Kuznecov and G. I. Kuznecov took part in carrying out the work.

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29. VI. 1937.

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CHEMISTRY

COMPOUNDS OF PLATINUM WITH UNSATURATED HYDROCARBONS OF THE ETHYLENE SERIES

By A. D. Gelman

(Communicated by N. S. Kurnakov, Member of the Academy, 4. VII. 1937)

In the writer's investigations carried out jointly with I. I. Černiajev ([1], [2]) it has been established that ethylenes, being in the inner sphere, exert a great trans-influence, so that ethylene compounds do not obey the fundamental laws of the chemistry of complex compounds, the Peyronnet law or the Reise law. By taking advantage of the law of trans-influence, we have succeeded in developing a method of obtaining three-dimensional isomers of compounds having the composition $[PtNH_3C_2H_4Cl_2]$ and $[PtPyC_2H_4Cl_2]$.

The facts ascertained had to be verified on other objects, so as to show that they were not purely fortuitous, but obeyed a definite law and were connected with the unsaturated structure of the substituent.

The best way to achieve that end was the gradual replacement of the substituents of the inner sphere of ethylehe compounds by their analogues replacing chlorine by bromine, and ethylene by propylene, butylene phenylethylene.

The conditions under which these compounds were obtained were the same as in the case of chlorides (l. c.), the trans-form being obtained from salts of the Zeise type; and the cis-form from salts of the Coss type. The first

Table 1

$[PtC_2H_4NH_3Br_2]$

Property	Cis-isomer	Trans-isomer
Colour	Bright yellow	Yellow
Solubility in water at 25°C	0.226 g in 100 cm³ of solution	0.103 g in 100 cm³ of solution
Solubility in C_2H_5OH at 25°C	0.136 g in 100 cm³ of solution	0.407 g in 100 cm³ of solution
Behaviour towards $AgNO_3$	Cloudiness appears instantly and AgCl settles	Faint opalescence, no precipitate
Behaviour towards HCl in the cold	Does not dissolve	Forms $NH_4[PtEtClBr_3]$
Behaviour towards $SC(NH_2)_2$	Forms $Pt4SC(NH_2)_2Br_2$	Forms $Pt4SC(NH_2)_2Br_2$
Behaviour to heating of aqueous solution	Decomposes after boiling for 5 or 6 min.	Decomposes after boiling for 2 or 3 min.
Behaviour to heating of dry substance	Decomposes at 167.5°	Decomposes at 138—138.5°

to be synthesized were platinum ethylene bromides. They are readily obtainable by heating the chlorides in question with potassium bromide. Tables 1 and 2 show the characteristics of platinum ethyleneamindibromides.

Table 2

$[PtC_2H_4C_5H_5NBr_2]$

Property	Cis-isomer	Trans-isomer
Colour	Orange-yellow	Dark yellow
Solubility in water at 25°C	0.065 g in 100 cm³ of solution	0.020 g in 100 cm³ of solution
Solubility in C_2H_5OH at 25°C	Does not dissolve	0.451 g in 100 cm³ of solution
Behaviour towards $AgNO_3$ in the cold	Yields a precipitate of AgCl	No precipitate
Behaviour towards HCl in the cold	Does not dissolve	Dissolves and forms PyH [$PtEtBr_2Cl$]
Behaviour towards $SC(NH_2)_2$	Forms $Pt4SC(NH_2)_2Br_2$	Forms $Pt4SC(NH_2)_2Br_2$
Behaviour to heating of aqueous solution	Decomposes partly after boiling for 9—10 min.	Decomposes upon boiling for 2—3 min.
Behaviour to heating of dry substance	Decomposes at 159.5°—160°	Decomposes at 118—118.5°

The reactions:

$$Me_2\left[\begin{matrix}Cl & Cl\\ & Pt\\ Cl & Cl\end{matrix}\right] + C_nH_{2n} = Me[PtC_nH_{2n}Cl_3] + MeCl,$$

where $C_nH_{2n} = C_3H_6$, C_4H_8; $Me = K^+$, NH_4^+, proceed smoothly in the cold for several days.

The ammonia and pyridine dichlorides of composition $[PtC_3H_6NH_3Cl_2]$ and $[PtC_3H_6PyCl_2]$ respectively, precipitated out of Zeise's propylene salt, are quite similar as to properties to the corresponding ethylene compounds but less stable than the latter.

The attempt to crystallize out the butylene compounds obtained by M. M. Bauman proved unsuccessful but the whole of their behaviour is reminiscent of propylene chlorides.

The treatment with propylene of an aqueous solution of Coss salt failed to separate the cis-dichloride. Out of an alcohol solution propylene separates a scanty bright yellow residue which could not be studied in detail owing to the slender yield. The same refers to butylene.

The reaction with styrol proceeds with exceptional smoothness (in an alcohol-aqueous solution in the cold):

1. $Me_2[PtCl_4] + C_8H_8 = Me[PtC_8H_8NH_3Cl_2]$.
2. $Me_2[PtC_8H_8Cl_3] + NH_3 = [PtC_8H_8NH_3Cl_2] + MeCl$.

The first reaction always yields, besides the soluble $Me[PtC_8H_8Cl_3]$ salt, an insoluble by-product of composition $[PtC_8H_8Cl_2]_2$. Its yield is 12—15% of the theoretical value. That compound had, it is true, been obtained under other circumstances and described by M. S. Kharasch and Ashford (Americans) [3] and also by S. Anderson (English) [4] in 1936. The treatment of $[PtC_8H_8Cl_2]_2$ with styrol failed to yield any distyroldichloride of platinum, $[Pt2C_8H_8Cl_2]$. This casts a doubt on S. Anderson's (l. c.) statement that the treatment of $[PtC_2H_4Cl_2]$ with styrol yields $[PtC_8H_8Cl_2]_2$ with a considerable admixture of $[Pt(C_8H_8)_2Cl_2]$. It is to be supposed that a mistake had been made in the analysis. The author's object was to determine the

platinum content only and, having obtained a rather low percentage of the latter, he put down the fact to an admixture of $[Pt(C_8H_8)_2Cl_2]$. The analysis of the $[PtC_8H_8Cl_2]_2$ compound for Pt should be made with the greatest possible care, as a certain percentage of platinum is, otherwise, lost; the determination of the chlorine content, however, always gives good results.

By adding ammonia to Zeise's phenylethylene salt, platinum phenylethyleneaminochloride was obtained. The treatment of Coss's salt with styrol yielded a compound of an identical composition.

Table 3 shows that the phenylethylene aminochlorides of platinum exist in the same two forms as the ethylene ones.

Table 3

$[PtC_8H_8NH_3Cl_2]$

Property	Cis-isomer	Trans-isomer
Colour	Pale yellow	Yellow
Solubility in water at 25°C	Does not dissolve	0.007 g in 100 cm³ ot solution
Solubility in C_2H_5OH at 25°C	0.119 g in 100 cm³ of solution	0.746 g in 100 cm³ of solution
Behaviour towards $AgNO_3$ in the cold	Yields a precipitate of AgCl	Faint opalescence after 5—7 min.
Behaviour towards HCl in the cold	Does not dissolve	Dissolves and forms $NH_4[PtC_8H_8Cl_3]$
Behaviour towards $SC(NH_2)_2$	Forms $Pt_4SC(NH_2)_2Cl_2$	Forms $Pt_4SC(NH_2)_2Cl_2$
Behaviour to heating of aqueous solution	Begins to decompose after 20—25 min. of boiling	Begins to decompose after 15 min. of boiling
Behaviour to heating of dry substance	Decomposes at 178°	Decomposes at 134—135°

The above facts indicate that the unsaturated hydrocarbons of the ethylene series, when entering the complex molecule, do actually exert a great trans-influence. These facts also confirm the statement made by us previously (l. c.), viz. that no three-dimensional isomers of these compounds can be obtained except by changing the order in which amines and unsaturated hydrocarbons are introduced into the inner sphere.

In boiling $[PtNH_3C_2H_4Cl_2]$ (cis) with 10—12% HCl for 15—20 min. the substance became gradually dissolved. Upon cooling, only part of the substance separated unchanged, most of it remaining in the solution. Either Zeise's or Coss's salt was to be expected to appear in the filtrate. If Zeise's salt had been found it might have been made to yield $[PtNH_3C_2H_4Cl_2]$ transforms by treating it with ammonia.

The filtrate, however, yielded no precipitate with either ammonia or pyridine. With Reise's salt of the former base an abundant bright yellow residue was precipitated. Analysis showed that we had to do with $[Pt(NH_3)_4]$ $[PtNH_3Cl_3]_2$, i. e. that the filtrate contained Coss's salt, not Zeise's salt. Consequently, this is how the reactions proceeded:

$$1.\ \left[\begin{matrix} C_2H_4 & Cl \\ & Pt \\ NH_3 & Cl \end{matrix}\right] + HCl \rightarrow H\left[\begin{matrix} Cl & Cl \\ & Pt \\ NH_3 & Cl \end{matrix}\right] + C_2H_4.$$

$$2.\ 2H\left[\begin{matrix} Cl & Cl \\ & Pt \\ NH_3 & Cl \end{matrix}\right] + (NH_3)_4PtCl_2 = [Pt(NH_3)_4][PtNH_3Cl_3]_2.$$

This fact is highly significant for the characteristic of ethylene as a substituent. On the one hand, ethylene carries a high trans-influence, on the other, it is easily displaced in a compound by the action of an excess of ammonia or pyridine, or by boiling with a strong solution of hydrochloric acid.

A special experiment has shown that ethylene displaces propylene and isobutylene in their platinum compounds, being itself displaced by styrol in the cold, at ordinary pressure. The reaction of displacement of propylene by styrol proceeds with especial rapidity.

Curiously enough, iso-butylene displaces propylene, which is in turn displaced by iso-butylene, thus, the capacity of unsaturated combination decreases in the following order:

$$C_8H_8 > C_2H_4 > C_3H_6 \approx C_4H_8.$$

The reasons advanced by S. Anderson (l. c.) in favour of placing ethylene before styrol as regards capacity for coordinated combination do not seem to me entirely convincing.

Conclusions

Both the papers cited above and the present investigation allow us, as it seems, even now to express the laws of trans-influence in a more general formula than that given by I. I. Černiajev in 1926. We must namely consider that place in the inner sphere to be of the highest reactivity which is in the trans-position to the active substituent. Such active substituents (i. e. possessing a high trans-influence) may be not only acid groups (old version), but also such molecules as thiourea, ethylene, propylene, butylene, styrol, etc.

Carbon monoxide will also take up a place in this series. Further investigations may be expected to bring to light an increasing number of such molecules.

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4. VII. 1937.

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GÉOCHIMIE

LA SÉRIE ISOMORPHE-KÉROLITE-BEIDELLITE DANS LES SILICATES ARGILEUX

Par D. P. SERDIUČENKO

(Présenté par V. I. Vernadskij, de l' Académie, le 11. VI. 1937)

Parmi les minéraux d'argile nous établissons pour la première fois la présence de la série isomorphe kérolite-beidellite.

En 1874 A. Damour et Salvétat (1) ont décrit du gisement Montmorillon (Vienne) en France un minéral savonneux de couleur rose foncée ayant selon R. E. Grim (2)

$$N_g = 1.527;\ N_p = 1.503;\ N_g - N_p = 0.024.$$

Les analyses faites par les auteurs sus-cités, A. Damour et Salvétat, ont montré une composition typique de la montmorillonite correspondant aux formules:

d'après l'analyse 1: $0.16\,RO \cdot Al_2O_3 \cdot 4.15\,SiO_2 \cdot 7.19\,H_2O$,
» » 2: $0.15\,RO \cdot Al_2O_3 \cdot 4.12\,SiO_2 \cdot 7.14\,H_2O$.

Plus tard, C. Ross et E. Shannon (3) et presque en même temps G. Calsow (4) ont examiné des montmorillonites prélevées du même gîte, de la composition suivante:

3—d'après l'analyse de Shannon; 4—d'après l'analyse de Calsow.

Les composants	3		4	
	%	Membre moléculaire	%	Membre moléculaire
SiO_2	48.60	8092	48.94	8151
Al_2O_3	20.03	1965	24.17	2371
Fe_2O_3	1.25	78	1.44	91
FeO	—	—	—	—
MnO	0.16	—	—	—
MgO	5.24	1300	2.18	540
CaO	1.72	307	1.00	179
H_2O	21.52	11942	21.96	12200
	98.52	—	99.69	—

Les formules des minéraux calculées par nous sont:

d'après l'analyse 3: $0.78\,RO \cdot R_2O_3 \cdot 3.96\,SiO_2 \cdot 5.84\,H_2O$.
» » 4: $0.29\,RO \cdot R_2O_3 \cdot 3.30\,SiO_2 \cdot 4.95\,H_2O$.

L'analyse 3 se distingue essentiellement de la norme admise pour la montmorillonite par la grande teneur de R″O, tandis que l'analyse 4 montre une relation des oxydes bien pareille à celle de la beidellite.

En examinant les analyses 3 et 4 ensemble nous trouvons qu'avec un contenu égal de H_2O et SiO_2 elles ont des relations inversement proportionnelles de Al_2O_3 et MgO, c'est-à-dire, que selon la loi de valence les deux derniers éléments se remplacent mutuellement au point de vue isomorphe.

Nous donnons le calcul de l'extrême terme magnésien de la série isomorphe d'après les deux analyses:

d'après l'analyse 3: $RO \cdot 1.05\,SiO_2 \cdot 1.54\,H_2O$,

» » 4: $RO \cdot 1.00\,SiO_2 \cdot 1.50\,H_2O$.

Nous avons obtenu de la sorte la composition idéale de la k é r o l i t e.

Nous allons déterminer l'extrême membre alumineux de la série isomorphe:

d'après l'analyse 3: $R''_2O_3 \cdot 3.14\,SiO_2 \cdot 4.64\,H_2O$,

» » 4: $R''_2O_3 \cdot 3.00\,SiO_2 \cdot 4.50\,H_2O$.

Nous avons obtenu ainsi la composition idéale de la b e i d e l l i t e.

Nous constations que les minéraux argileux du gisement Montmorillon, étroitement liés les uns avec les autres de par leur génèse, représentent ou a) des montmorillonites typiques ou bien b) divers mélanges isomorphes, selon la quantité des composants extrêmes, de la série kérolite-beidellite.

A. E. Fersmann ([5],[6]) a décrit un minéral argileux qu'il avait découvert en 1905 dans la carrière de basalte Roth (Rhön), près de la station Nordheim, présentant un remplissement des crevasses entre des colonnes isolées phonolithiques de basalte.

Le minéral est d'une couleur rose-claire, assez moelleux, se désagrégeant dans l'eau. Devant un tuyau à souder le minéral fond en émail blanc. Dans H_2SO_4 le minéral se désagrège complètement sous sécrétion de SiO_2 en état pulvérulent; HCl agit sur lui faiblement et avec lenteur.

Le minéral est rapporté par l'auteur au groupe de montmorillonites représentant un produit de la destruction du basalte.

F. Heide* ([7]) a indiqué en 1927 que dans les carrières de basalte phonolithique (Unter-Rupsroth, Rhön), quelques kilomètres à l'est de Milseburg, se trouve en abondance un minéral argileux de couleur rose qui, selon les données de l'examen microscopique et chimique, doit être rapporté au groupe des montmorillonites. Dans les phonolithes à forme de colonnes le minéral forme ou des filons menus (jusqu'à 10 cm d'épaisseur) ou bien il y remplit des vacuités amygdaliennes conjointement avec la calcite, la schabasite, la natrolite et l'analcime. Dans ces deux cas la phonolithe qui confine à la montmorillonite, est tout à fait fraiche et ne se trouve pas en état de désagrégation.

Sous microscope le minéral apparaît de différentes couleurs du rougeâtre à l'incolore; il est à bifraction considérable, n'est pas pléochroïque, avec de toutes petites feuillettes et des fibres, parallèlement à l'élongation desquelles se trouve le N_g.

Ayant été gardé dans la chambre pendant deux années, le minéral possède $n=1.545\pm0.006$.

Par HCl le minéral se désagrège faiblement, et par H_2SO_4, d'une manière plus intense.

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* F. Heide ne fait pas mention de l'œuvre de A. E. Fersmann qui le premier a découvert et examiné le minéral argileux de couleur rose, de Rhön.

La composition chimique du minéral prélevé sous microscope:

1—d'après l'analyse de F. Heide; 2—d'après l'analyse de A. E. Fersmann.

Les composants	1		2	
	%	Membre moléculaire	%	Membre moléculaire
SiO_2	49.21	8193	48.54	8081
TiO_2	Absent	—	—	—
Al_2O_3	22.61	2216	19.38	1901
Fe_2O_3	0.43	26	0.20	12
MnO	Traces	—	—	—
CaO	1.95	344	1.07	172
MgO	2.13	528	5.29	1322
K_2O	Traces	—	Traces	—
Na_2O	0.45	—		
P_2O_5	Absent	—	—	—
CO_2	Absent	—	—	—
$+H_2O$	9.34	5188	8.94	4966
$-H_2O$	14.37	7983	16.81	9338
	100.49	—	100.23	—

Formules du minéral:

d'après l'analyse 1: $0.39\,R''O \cdot Al_2O_3 \cdot 3.66\,SiO_2 \cdot 2.31\,H_2O + 3.56\,H_2O$,
» » 2: $0.78\,R''O \cdot Al_2O_3 \cdot 4.22\,SiO_2 \cdot 2.53\,H_2O + 5.00\,H_2O$.

La teneur en SiO_2 et H_2O est presque égale dans les deux analyses, tandis que les quantités de Al_2O_3 et MgO s'y trouvent dans une relation inversement proportionnelle.

L'une et l'autre des analyses du minéral argileux de couleur rose du basalte Rhön montrent des substances analogues quant à leur nature et à leur génèse, avec la présence en elles des substitutions isomorphes $3\,Mg \rightarrow Al_2$.

Si nous substituons d'une façon équivalente tout le RO par Al_2O_3 dans les analyses de F. Heide (1) et de A. E. Fersmann (2), nous obtiendrons des formules presque identiques d'un minéral d'aluminium correspondant à la beidellite:

d'après l'analyse 1: $Al_2O_3 \cdot 3.24\,SiO_2 \cdot 2.04\,H_2O + 3.15\,H_2O$,
» » 2: $Al_2O_3 \cdot 3.35\,SiO_2 \cdot 2.00\,H_2O + 3.10\,H_2O$.

Si nous substituons tout le Al_2O_3 par une quantité équivalente de MgO, nous obtiendrons en résultat des formules parfaitement égales d'un minéral magnésial correspondant à la kérolite:

d'après l'analyse 1: $RO \cdot 1.08\,SiO_2 \cdot 0.68\,H_2O + 1.04\,H_2O$,
» » 2: $RO \cdot 1.11\,SiO_2 \cdot 0.69\,H_2O + 1.28\,H_2O$.

Nous voyons de la sorte que les minéraux de Rhön présentent des membres de la série kérolite-beidellite. Le superflu du silice dans les formules kérolite-beidellite s'explique dans notre cas, à ce qu'il paraît, par l'addition isomorphe de la montmorillonite.

Dans les substitutions isomorphes $Al_2—3\,Mg$, la série kérolite-beidellite a la forme:

$$3MgO \cdot 3\,SiO_2 \cdot 4.5\,H_2O — Al_2O_3 \cdot 3SiO_2 \cdot 5H_2O.$$

D'après l'examen de J. W. Gruner (8) et C. E. Marshall (9), la structure roentgénienne de la beidellite, nontronite et montmorillonite est presque identique; ces minéraux forment une série isomorphe.

Il est tout à fait évident qu' étant donné les relations isomorphes: 1) entre la beidellite et la montmorillonite et 2) entre la beidellite et la kérolite, les mêmes relations doivent également subsister entre la kérolite et la montmorillonite.

Les minéraux de Rhön servent d'exemple de telles relations isomorphes complexes.

Nous avons déjà indiqué(10) que certains silicates argileux (SiO_2:Al_2O_3=4) contenant MgO jusqu'à une unité moléculaire, représentent possiblement un silicate «consistant d'un noyau silicieux magnésial (type kérolite) et de beidellite dans la chaîne latérale».

Nous croyons bien que ce «produit d'addition » dans nombre de cas doit être considéré comme membre (le plus stable?) de la série kérolite-beidellite isomorphe.

Cabinet de Minéralogie et de Pétrographie
à l'Université de Rostov.

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BIOCHEMIE

OXYDO-REDUKTIONS-POTENTIAL BEI DER PEPSINVERDAUUNG DES PROTEINS

Von A. N. ADOWA und I. A. SMOPODINZEW

(Vorgelegt von A. A. Richter, Mitglied der Akademie, d. 7. VII. 1937)

Nachdem die grosse Bedeutung der aktiven Reaktion des Mediums für die Untersuchung der fermentativen und anderen biologischen Prozessen festgestellt worden war, traten das Oxydo-Reduktions-Potential und rH in den Vordergrund, als Faktoren die zur Begreifung und Erklärung vieler biochemischen Prozesse wesentlich beitragen. Während pH ein Gleichgewicht zwischen H und OH-Ionen darstellt, zeigt rH demgegenüber dasjenige zwischen molekularem Sauerstoff und Wasserstoff an und Eh bringt die Beziehung zwischen den obenerwähnten Gleichgewichte zum Ausdruck. Viele Autoren sind der Ansicht, dass bei der Pepsinverdauung mit der Zerlegung der Peptid-Gruppen auch die Zerlegung anderer, noch nicht bekannten Verbindungen vor sich gehe. Um ins reine zu bringen, ob sich dabei ein elektrodynamischer Prozess vollzieht, haben wir die Veränderung des rH in dem Gemische des Eiweisses mit Pepsin im Laufe von 24—72 Stunden untersucht.

Untersuchungsmethode

Eine 5%-ige Lösung von Kasein (1) oder Gelatine wird mit dem gleichem Volumen einer 1%-gen Lösung von Pepsin vermischt und in das Gemisch sofort die Platinelektroden eingetaucht, um das Oxydo-Reduktions-Potential bei Zimmertemperatur zu messen. Dann setzt man das Gefäss mit den Elektroden in den Brutschrank bei $t=39—40°$. Nach jeder Stunde wird das Gemisch abgekühlt und das Potential gemessen. In demselben Gemisch bestimmt man gleichzeitig das pH mit Hilfe der Chinhydron-Elektrode.

Man berechnet nach der Formel:

$$\mathrm{Eh} = E_0 + \frac{RT}{nF} \cdot \ln \frac{[\mathrm{ox}]}{[\mathrm{red}]}, \qquad (1)$$

$$\mathrm{Eh} = 0.029\,[\mathrm{rH} - 2\mathrm{pH}]. \qquad (2)$$

Daraus folgt:

$$\mathrm{rH} = \frac{\mathrm{Eh}}{0.029} + 2\mathrm{pH}. \qquad (3)$$

Zuerst bestimmten wir das Oxydo-Reduktions-Potential in den Ausgangslösungen—in den Lösungen des Kaseins (bzw. Gelatine) und den zwei Fermentlösungen (einer starken № 2 und einer schwachen № 22) (2).

Tabelle 1

Oxydo-Reduktions-Potential der Ausgangslösungen

	0			Nach 1 Stunde			Nach 3 Stunden			Nach 24 Stunden		
	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh
Starkes Pepsin-Präparat № 2	1.26	20	0.51	1.26	22	0.58	1.21	22	0.58	1.21	22	0.58
	1.26	21	0.52	1.26	22	0.58	1.21	22	0.58	1.21	22	0.58
Schwaches Pepsin-Präparat № 22	0.894	23.7	0.64	0.98	24.5	0.66	0.982	25	0.67	0.84	24.2	0.65
	1.896	23.9	0.64	0.982	24.7	0.66	0.982	25	0.67	0.84	24.2	0.65
5%-ige Gelatinelösung	5.177	21	0.33	5.177	21	0.32	5.177	21	0.32	5.263	21	0.32
	5.177	21	0.33	5.177	21	0.32	5.177	21	0.32	5.263	21	0.32
5%-ige Kaseinlösung	7.637	29.2	0.40	7.637	30	0.44	7.637	30	0.43	7.637	30	0.44
	7.637	30.2	0.43	7.637	30.2	0.43	7.637	30.2	0.43	7.637	30.5	0.44

Aus der Tab. 1 ersieht man, dass Eh schwacher Fermentlösung um 0.12 bis 0.13 v höher ist als bei der starken Fermentlösung, ebenso ist Eh in der Kaseinlösung um 0.07—0.10 v höher als in der Gelatinelösung; sowohl in der Lösung des Fermentes wie auch in jener der Proteine war das Oxydo-Reduktions-Potential nach einer Stunde stabil. Es verändert sich im Laufe längerer Zeit nicht (z. B. nach 72 Stunden beim Versuch mit Pepsin № 2).

Bei der Mischung des Kaseins mit einer Lösung des starken Fermentes № 2 verminderte sich das rH während einer Stunde bis zu der Grösse rH des Pepsins und war nach 24 Stunden etwas höher, ebenso wie Eh.

Bei der Mischung des Kaseins mit einer Lösung des schwachen Fermentes № 22, wird das rH der Mischung nach Verlauf einer Stunde etwas niedriger als die Grösse des rH der Fermentlösung. Nach drei Stunden wird das Eh niedriger als es in ungelöstem Ferment ist und bleibt im Laufe von 24 Stunden unverändert. Wenn ein gekochtes Ferment № 22 gebraucht wird, erhalten rH und Eh einen etwas höheren Wert. Bei dem starken Ferment № 2, ist zwischen rH und Eh der gekochten und nichtgekochten Lösung kein Unterschied zu bemerken (Tab. 2).

Tabelle 2

Oxydo-Reduktions-Potential bei der Pepsinverdauung des Kaseins

	Sogleich nach der Mischung			Nach 1 Stunde			Nach 3 Stunden			Nach 24 Stunden		
	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh
Kasein und starkes Pepsin № 2	1.416	20.5	0.51	1.432	22	0.55	1.433	22	0.56	1.792	23	0.57
	1.416	20.5	0.51	1.433	22	0.55	1.433	22	0.56	1.792	23	0.57
Kasein+gekochtes Pepsin № 2	1.537	20.6	0.51	1.537	22.3	0.54	1.537	22	0.56	1.485	23	0.56
	1.537	20.8	0.51	1.537	22.5	0.54	1.537	22	0.55	1.485	22.9	0.56
Kasein+schwaches Pepsin № 22	1.572	21.5	0.53	1.537	22.5	0.56	1.537	23.4	0.59	1.624	23	0.59
	1.572	20.8	0.51	1.537	22.5	0.56	1.537	23.4	0.59	1.624	23	0.59
Kasein+gekochtes Pepsin № 22	1.485	21.0	0.52	1.485	24	0.61	1.485	24.8	0.63	1.416	24.7	0.63
	1.485	21.2	0.53	1.485	25	0.64	1.485	25.6	0.66	1.416	25.5	0.65

Diese Ergebnisse erlauben doch nicht zu behaupten, dass in der Luftatmosphäre, bei der Pepsinverdauung des Kaseins, ein elektro-dynamischer Prozess vor sich gehe. Dem mehr aktiven Fermente in dem Gemische entspricht eine kleine Verminderung von Eh.

Bei der Mischung der Gelatine mit den Lösungen des starken und des schwachen Fermentes vermindert sich das rH mehr als beim Eiweiss, bis zu einem Niveau, das für beide Fermente dasselbe ist, dann aber wird sofort stabil, und im Laufe von 72 Stunden der Verdauung (Tab. 3) verändert sich nicht.

Tabelle 3

Oxydo-Reduktions-Potential bei der Pepsinverdauung der Gelatine

	Sogleich nach der Mischung			Nach 1 Stunde			Nach 3 Stunden			Nach 24 Stunden		
	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh	pH	rH	Eh
Gelatine+starkes Pepsin № 2	1.26	19.5	0.49	1.26	19.5	0.49	1.26	19.5	0.48	1.26	19.5	0.48
	1.26	19.5	0.49	1.26	19.5	0.49	1.26	19.5	0.48	1.26	19.5	0.48
Gelatine+gekochtes Pepsin № 2	1.364	19	0.48	1.329	19	0.47	1.329	19	0.47	1.312	20	0.51
	1.364	19	0.48	1.329	19	0.46	1.329	19	0.47	1.312	20	0.51
Gelatine+starkes Pepsin № 22	1.365	19.2	0.48	1.273	19	0.47	1.275	19	0.48	1.26	20	0.50
	1.365	19.1	0.48	1.275	19	0.46	1.275	19	0.47	1.263	19.8	0.51
Gelatine+gekochtes Pepsin № 22	1.346	19.3	0.48	1.277	18.9	0.47	1.277	18.9	0.48	1.26	19.6	0.50
	1.346	19.4	0.49	1.277	18.9	0.48	1.277	18.9	0.48	1.26	19.4	0.49

Aus unseren früheren Untersuchungen (1) geht hervor, dass beim Titrieren der Verdauungsprodukte des Kaseins gewöhnlich mehr Alkali als bei der Gelatine verbraucht wird. Wenn dies auf eine leichtere Verdaulichkeit des Kaseins zeigen sollte, so ist dieselbe von einem grösseren Wert des rH beim Kasein begleitet.

Schlussfolgerungen

1. Bei der Pepsinverdauung der Eiweisse findet kein elektro-dynamischer Prozess statt.

2. Der leichteren Pepsinverdauung des Kaseins, im Vergleich mit der Gelatine, entsprachen etwas höhere Werte von rH.

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GEOLOGY

A NEW TUNGSTEN-BEARING REGION IN THE USSR

By N. I. NAKOVNIK

(Communicated by A. D. Archangelskij, Member of the Academy, 15. XII. 1936)

The tungsten-bearing possibilities of Kazakh steppe did not come to light until 1931, when a number of mineralized wolframite deposits were successively discovered in the granite fields. The first find of wolframite, which dates back to 1925, had only a mineralogical interest. Up to 1936, three such discoveries are on record: Kuzyu-Adir, 240 km south of Karaganda, Kizil-tau, 300 km south-west of the same point, and quartz hills on the Kounrad, 6 km east of the copper ore field. The last mentioned discovery, made in 1934 by the writer of these lines, was the largest, and furnished an inducement to start research and prospecting work in the steppe. It is a matter of regret that, up to the present, this work has been confined to the Kounrad district, although all the conditions necessary for its wide extension seem to be available. I emphasized this fact as far back as two years ago, while putting forward the problem of rare metal ores on the granites of Kazakh steppe (1).

In the current year, the writer and his co-workers, who took part in the Expedition of the Geological Institute of the Academy of Sciences and the Council for the Study of Natural Resources, were enabled to carry out extensive research work on the massifs of secondary quartzites in the hilly part of the steppe, i. e. in a vast and, geologically speaking, its most promising region. I made use of the facilities thus afforded for a simultaneous examination of the granite fields with a view to ascertaining the presence of tungsten ore or of other rare metal ores.

The results of my investigations confirmed my previously formulated supposition as to the probability of more frequent occurrences of tungsten in the granite field of Kazakh steppe and the possibility of encountering it in commercial quantities.

These results are as follows:

1. In surveying the periphery of Karkaralinsk granite massif, I. I. Pankul, my assistant, and myself, discovered, at 2 km from the town of Karkaralinsk at two different points, an occurrence of tungsten mineralized into wolframite. It is associated with the endocontact zone and is imbedded in thin quartz veinlets, accompanied by micaceo-fluoritic greisens. The first mineralized area measures about 200×200 m, the second, 20×20 m. The industrial value of either of them is far difficult to ascertain; the only thing that has been made clear is that the short stretch (some 4 km in length) of the edge of the massif cursorily examined by the writer seems to epitomize the geo-

logical conditions of the rest of its periphery extending over 65 km, and that a more detailed survey might reveal both mineralized areas and the presence of tungsten in industrial quantities.

2. The discovery of wolframite in the Karkaralinsk mountains prompted my assistants to double their efforts in searching the granite fields for rare metals. Hardly a month had elapsed since the date of the first find, when the geologist A. S. Osipov discovered a fairly large tungsten deposit to the north-west of Balkhash lake, namely 80 km to the north of Kizil-Espe and 80 km east of the Karaganda—Balkhash railway, in Kiziltau mountains. Another examination made by him jointly with myself resulted in the discovery of a second area (at the foot of Akchetau Mountain) lying 2 km south-east of the first and of a much smaller size, but very promising as regards the length of the ore veins and the high content of the ore mineral. The total area of the whole deposit is about 12 km².

The ore-field lies within the endocontact zone of the granites with metamorphic argillaceous shales. The mineralized wolframite is imbedded in quartz veins which intersect the granites and the metamorphic argillaceous shales. Along the quartz veins the granites have been metamorphosed into micaceo-fluoritic greisens. As to the metamorphic argillaceous shales, they are found to have been bleached in their immediate contact with the quartz veins and are now a quartzose muscovite rock. The thickness of the quartz veins does not exceed 25—30 cm at most; as a rule, they are much thinner (2—5 — 10 cm) and intersect the greisens at an acute angle, having an uniformly meridian or nearly meridian strike.

The greisens are very extensively developed, their thickness being in places 15—20 m. The processes of erosion have segregated these rocks from the embedding granites into rectilinear lenticular seams of as much as 1—1.5 km in length. The average length of these greisen veins is 400—500 km. Veins of 200 m in lenght are but rarely encountered.

A highly valuable find, which greatly enhances the interest afforded by the newly discovered deposit, is the discovery, in the second area, of mineralized beryllium with crystals of aquamarine, some of which are 3—4 cm in length, and also the discovery of molybdenite and tourmaline in the quartz veins of the central part of the deposit.

As regards the genesis of the deposit, it may by stated to bear unmistakable traces of hypothermal mineralization as evidenced both by the ores themselves and by the accompanying vein minerals and lateral alterations.

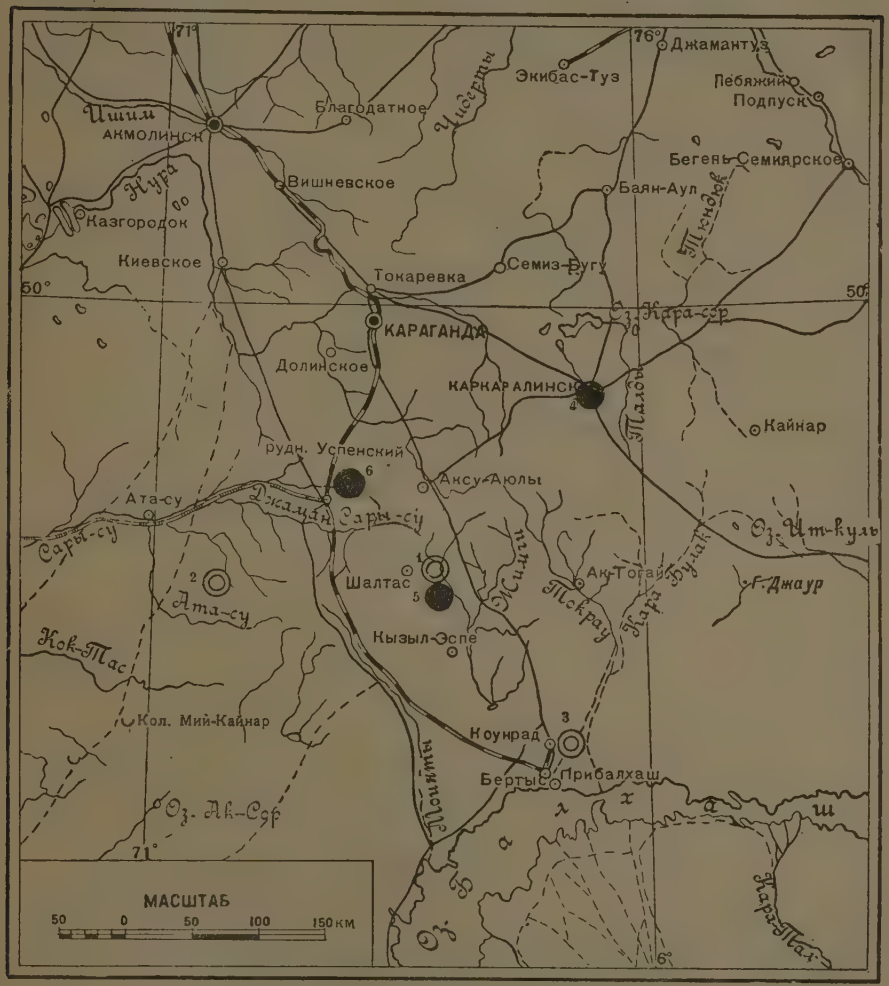
The consistent rectilinearity of the veins, the well-defined greisen areas, the simple and gentle relief, the proximity of a railway line and of so important an industrial centre as Pribalkhashstroi,—all this, combined with the size of the mineralized areas mentioned above, gives an undoubted industrial value to the newly-discovered deposit, not to mention the great scientific interest afforded by its beryllium rocks and by other minerals it contains and which have so far not been studied.

The only thing that might place economic difficulties in the way of a successful prospecting and working of the deposit is the insufficiency of natural waters.

3. A third deposit was discovered by the geologist V. N. Popov at a distance of 18 km to the north-east of Uspenski Mine. Wolframite was found in the debris near the vein and was also identified in the quartz rock in situ, as a brownish earthy mass remaining after lixiviation.

4. To the three discoveries made this year, a fourth one ought to be added, namely the granite field of Kizil-tau lying 150 km north of Kounrad and abounding in quartz veins with fluoritic greisens. The whole of that field ought to be throughly examined; no such examination, however, could be made

SURVEY OF TUNGSTEN OCCURRING IN EAST KASAKHSTAN



TUNGUSTEN-BEARING LOCALITIES

- Discovered in 1936
- Previously discovered
- River beds
- Towns
- Other populated localities
- 1 – Kuzjuadir (Кузжадыр)
- 2 – Kiziltau (Кызылтау)
- 3 – Kounrad (Коунрад)
- 4 – Karkaralinsk (Каркаралинское)
- 5 – Akchetau – Kizil – Tas (Акчетау – Кызыл – Тас)
- 6 – In the region of the Uspenski mine (Успенский)
- Railways
- Amel. unpaved highways
- pathways

this year owing to lack of time. All the granite fields to the north-west of Balkhash lake and more especially those situated around Kizil-Espe are highly promising in respect of discoveries of tungsten.

If all the finds of tungsten ores so far known were to be mapped and if the discoveries made this year and all the points where indications of the occurrence of such ores are to be found were added thereto, there would be outlined an extensive tungsten-bearing region gravitating towards the Karaganda—Balkhash railway.

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MINERALOGY

QUANTITATIVE MINERALOGICAL X-RAY ANALYSIS

By T. N. AGAFONOVA

(Communicated by S. I. Wawilow, Member of the Academy, 13. VII. 1937)

The quantitative X-ray analysis may be based on absolute as well as on relative intensities of the powder photograph lines.

The author considers that it is best to use relative intensities of powder photograph lines in quantitative mineralogical analysis.

The line intensities of a given substance may be calculated according to following formula:

$$I = [F(hkl)]^2 \cdot W \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos\theta} \cdot H \cdot K \ ,$$

where $[F(hkl)]^2$ is the structural factor,
W—Debaye's thermal factor,
$1+\cos^2 2\theta$—Thomson's polarization factor,
$\sin^2 \theta \cos \theta$—Lorentz's factor,
H—factor of repetition,
K—ratio coefficient.

In determining the relative line intensities on the same powder photograph taken at a constant wave length λ, all the above mentioned factors do not depend on the diffracting masses, being a function of the structural properties of the given substance.

Intensity variations due to variation of temperature conditions during the experiment, and not exceeding $\pm 5°$ C, may be neglected. The ratio coefficient K represents the total of all the peculiarities of an experiment not taken into account by the above enumerated factors (for instance: work of the X-ray tube, amount of the X-rayed material, dispersity rate, etc.). In obtaining powder photographs of mixtures $(A+B+C+\ldots+N)$ the conditions will be the same and the ratio $K_A : K_B : K_C : \ldots : K_N$ will depend mainly on the diffracting masses; consequently, it will be a function of the percentage (by weight) of each substance in the mixture. Thus, the relative line intensity of the diffraction spectrum of a mineral in the mixture is not directly proportional to its percentage (by weight) in this mixture; this dependence is much more complicated and can be determined only empirically.

The following method was applied by the author.

A certain quantity (usually not exceeding 10—15 p. c. by weight) of a standard substance (iron, aluminium, rock salt, etc.) is added to the mixture under investigation. The determination of the percentage content of the

mineral is based on the relative line intensity, i. e. on the comparative intensities of its spectrum and of that of the standard substance. The problem consists in determining the dependence of the percentage of the mineral in the mixture on the relative intensity of its lines in the spectrum.

For this purpose, we prepare a set of binar mixtures of a standard substance with the minerals investigated (content of the standard substance from 0 to 100 p. c., increasing gradually for every 4—5 p. c.) and take powder photographs. The exposure requires a direct ratio between film darkening and the energy absorbed. Then is determined the intensity ratio of two lines: of the standard substance «a» and of the mineral «b» for every mixture:

$$i_n = \frac{Ib(hkl)}{Ia(mno)}.$$

According to these data we obtain the comparative curve of relative line intensities for two lines of the mineral and the standard substance, forming part of the mixture. On the abscissa axis is plotted the percentage of the mineral «b» in the mixture, and on the ordinate axis the value

$$i = \frac{Ib(hkl)}{Ia(mno)}.$$

Such curves can be drawn for several pairs of sides, preference being given to those, easier for accurate determination. Lines of adequate intensity, noticeable even at a small content of the mineral in the mixture and set closely enough to reduce the influence of the background are chosen for comparison.

On obtaining X-ray picture of the investigated mixture we determine from its microphotogram

$$i_x = \frac{Ib(hkl)}{Ia(mno)}$$

for a pair of sides of the investigated mineral and of the standard substance, and find from the corresponding curve their ratio by weight. In as much as

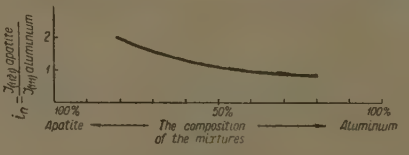

Fig. 1.

the content of the standard substance in the mixture is known in advance, it is easy to perform further calculations and to determine the percentage of the mineral in the mixture.

Fig. 1 represents the ratio curve of line intensities for apatite $(11\bar{2}1)$ and aluminium (111), corresponding to the composition of the mixtures. The origin of the coordinates for the abscissa axis corresponds to 100 p. c. (pure) apatite. In order to determine the apatite content in a mixture, one must add 10 p. c. of aluminium powder to this mixture, take an X-ray picture, determine the ratio

$$i_x = \frac{I\,(11\bar{2}1)\ \text{apatite}}{I\,(111)\ \text{aluminium}}$$

and find the corresponding ratio of apatite and aluminium, p/r.

Then the apatite content in the investigated mixture will be:

$$i_x = \frac{p}{r} \cdot 10 \text{ p. c. (by weight).}$$

The error in apatite determination by means of this curve varies from 2.5—6 p. c. The curve is based on 4 points, taken for every 20 p. c.

An interpolation between more closely distributed points on the curve should certainly reduce this error.

For instance, the curve in Fig. 2 represents the relative line intensities of pyrolusite (110) and braunite (222) corresponding to the composition of the mixtures; points are taken for every 10 p. c. and the error of the determi-

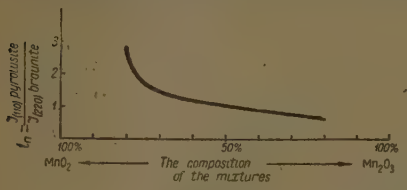

Fig. 2.

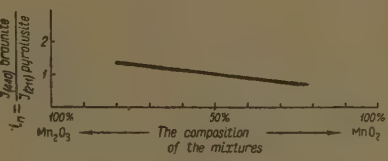

Fig. 3.

nation of pyrolusite in the mixture does not exceed 1 p. c., being reduced to 0.1 p. c. in the case of mixtures containing more than 60 p. c. of pyrolusite.

Fig. 3 shows a corresponding comparative curve for pyrolusite (211) and braunite (440) lines.

Errors in pyrolusite determination by means of this curve also do not exceed 1 p. c.

Curves 2 and 3 may be used for a direct determination of the composition of a binar mixture of pyrolusite and braunite.

The experiment was performed, in the usual Debaye cameras of the State Physical Technical Institute, recourse being had to a Hadding tube and a film made at the Uritsky factory being used.

Pictures of apatite-aluminium mixtures were taken with copper radiation ($\lambda K_\alpha = 1.539$ Å), and of braunite-pyrolusite ones with iron radiation ($\lambda K_\alpha = 1.933$ Å).

The use of precision instruments involving helicoidal motion, the measurement of diffraction spectra intensities by the ionization method and the reduction of the interpolation radius will considerably increase the accuracy of quantitative determinations of the mineral content in a mixture, but even the above described method is satisfactory for ordinary analyses.

The influence of the dispercity rate and the exposure on the accuracy of quantitative X-ray analyses should be the subject of special studies in the future.

The author expresses his gratitude to N. N. Padurov for valuable advise and to I. N. Maslenickij, Director of the Laboratory, for optimal conditions of research work in the course of his investigation.

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MINERALOGY

ALPINE TYPE VEINS IN THE URALS

By G. N. VERTUŠKOV

(Communicated by V. I. Vernadskij, Member of the Academy, 22. VI. 1937)

1. Minerals from Alpine type veins in the Urals have been known for a long time; beautiful crystals of albites, richly faceted apatites, and transparent calcites were mentioned by G. Rose as early as in the first half of the last century ([10]).

Epidote crystals from the Middle Urals, exceptional as to size, facets and colour, and known as «pushkinite», have now achieved a world-wide reputation thanks to the works of N. Kokšarov, E. Fedorov and others. Pebbles of transparent rock-crystals, with inclusions of tourmaline, epidote, tremolite and actinolite, termed «volosatiks» in the Urals, are every bit as beautiful as the St. Gothard crystals with inclusions of the same minerals, and are deservedly considered to be the best ornaments of the leading mineralogical museums in the USSR. Much useful and interesting work has been done in studying the crystallographic, chemical and other properties of various minerals found in the dry fissures of the Urals.

For some years past, it has been no secret to specialists interested in the mineralogy of the Urals and familiar with Alpine type veins not only from collection specimens, but also from the works of Koenigsberger and others, that the apatites, albites, epidotes etc. found in the Urals originate from local veins of the Alpine type (dry fissures), but no investigations of primary deposits of this type in the Urals have so far been made; the writer succeeded in discovering any only in 1930—1932, when he collected some promising material therefrom, which he classified under the guidance of Prof. K. K. Matvejev at the Mining Institute, Sverdlovsk.

2. In accordance with the views held by Koenigsberger ([6,7]), Niggli ([8]), Vernadskij ([1]) and Fersman ([12]), what we mean by Alpine type veins (dry fissures) are mineral formations of the lateral-secretory type, originated through the filling up from hot aqueous solutions* of open fissures and cavities of a dynamic origin occurring in various metamorphic rocks in zones of tectonic stress. The formation of Alpine type veins is one of the manifestations of metamorphic processes ([1]). Wherever tectonic shifts or other causes produce hollow fissures or cavities in rocks undergoing metamorphism, and mineralizers (CO_2, gaseous H_2O, possibly F or B compounds) are present in quantities ever so small, mineral veins will inevitably form in such fissures and cavities, the paragenesis of such minerals being mainly determined by the

* Or gaseous aerosols. *Acad. V. Vernadskij.*

chemical composition of the surrounding rock. Beautiful crystals of various silicates, oxides, carbonates, etc. are usually formed in this manner. The body of the vein is absent as a rule, but in acid and neutral rocks it is formed by milk-white quartz.

On the eastern slope of the Urals, in a region characterized by the most violent metamorphic processes, veins and fissures of the Alpine type were bound to arise in a variety of rocks and in metamorphized ore deposits. It is a matter for regret that up to the present only a few mineral formations occurring in fissures of metamorphic rocks have so far been studied from this point of view, but, following Koenigsberger's (7) example, we may already single out the following types of Alpine veins and class them according to the composition of the surrounding rocks:

a) veins included in greenstone shales,
b) veins in diallagites and peridotites,
c) veins in chromites.

3. Of the most common occurrence in the Urals are veins included in greenstone rocks containing pyrite beds. The outcrops of these rocks show in all their parts tiny veinlets usually runnig athwart the schistosity of the shales and containing plane-prismatic albite, dark-green prochlorite, epidote, tremolite and often quartz. Less frequently occur larger veins, of as much as several metres along the strike and 1 m thickness; these are apparently associated with some particular tectonic regions of the Urals. The writer has investigated in detail the veins discovered at Alexeyevskaya Gorka near Neivo-Rudyanka in Nevyanski district. Alexeyevskaya Gorka is made up of metamorphosed augitic porphyrites rent asunder by dykes of quartz albitophyres. On the western slope of the hill, coarse-grained epidoto-hornblende rocks crop out as dykes. This is where we discovered four veins of the Alpine type, the largest among them having the shape of a convexo-convex lens. Its strike is strictly latitudinal, its dip 20—30° south. Its length is 20 m along the strike, and 10 m along the dip, its thickness being up to 75 cm. The surrounding rocks within as much as 3 m of the vein have been strongly altered and converted into a friable porous mass consisting of minute grains of quartz, chlorite, epidote, and of some not fully identified grey kaolin-like mineral. This metamorphism differs entirely from that of the lateral rocks surrounding the auriferous-quartz veins of a meridional strike occurring in the same locality. Closely adhering to the Alpine type veins was a layer of prochlorite up to 10 cm thick. The body of the vein was composed to 80—90% of milk-white quartz with large cavities containing perfectly-shaped crystals of rock crystal up to 20 cm across and 40 cm long. This vein yielded as much as 500 kg rock crystals, most of which unfortunately contained numerous inclusions of fine-fibred tremolite. A full paragenesis of the minerals of the vein comprises quartz, pericline, tremolite, tourmaline, sphene, pyrites, prochlorite, and the secondary minerals: nontronite, pyrolusite, brown hematite. The most remarkable among these is sphene, which occurs in tabular crystals (102) with well developed (102) and (112) forms, while (100), (001) and (111) forms are poorly developed in penetration twins (100). Buff-coloured sphenes exactly similar to these are characteristic of the same type of veins in the Alps.

Some 60—70 m north of this vein a very small $3 \times 2 \times 0.2$ m vein having the shape of a very flat lens of a horizontal strike was tapped. The vein was a fissure the walls of which had been incrusted with following vein minerals: crystals of epidote, rock-crystal, fine-fibred tremolite, the void being filled with fine-scaled prochlorite. This vein yielded beautiful crystals of rock-crystal with inclusions of epidote and tremolite.

2 km north of Alexeyevskaya Gorka amid some schistose tuffs of augitic

porphyrites, there was discovered a vein containing absolutely transparent plane-prismatic crystals of albite, similar to those described by S. F. Glinka([4]); plane-prismatic brookites with (001), (100), (210), (110), (021), (124), (122), (104) sides developed; rutile, specular iron ore, muscovite, prochlorite and quartz, partly as well-formed crystals. A promising vein was found on Zaplotnaya Hill, 6—7 km S. W. of Neivo-Rudyanka. It contained radial concretions of desmine.

A comparison of the paragenesis of the minerals yielded by the investigated veins with the inclusions contained in the rock-crystal pebbles from the alluvial deposits of Neiva river, suggests a community of origin.

To that same type ought to be referred the Katsna Yama epidote deposit, famous throughout the Urals. It lies 15—16 km N. E. of Pervouralsk amidst epidotized porphyrites. It contains rock-crystal, epidote, sphene, tremolite, transparent tabular (0001) apatite, laumontite converted into β-leonhardite ([11]). In point of size and beauty of the crystals, the Katsna Yama epidotes hold their own with those of Knappenwand (Zalzburg Alps). Veins of the Alpine type appear to be widely distributed in this district, as evidenced by numerous rock-crystal pebbles similar to those encountered on Neiva river, in the alluvial deposit of Reshotka creek.

In the region round Myass, finds of brookite, anatase, and colourless albite have been known for a long time. In 1931 A. A. Murdasov supplied us with a specimen of rock-crystal found on Listvjanaya Hill, 8 km W. of Myass, and containing inclusions of albite, epidote, tremolite and prochlorite. This paragenesis proves beyond doubt that the specimen originated in an Alpine type vein.

Closely related to these veins are the veins of the abandoned Kiryabinsk copper mine, 80 km S. W. of Myass. The paragenesis of the minerals yielded by these veins is as follows ([10]): actinolite, albite, apatite, calcite, chlorite, malachite and azurite.

4. The Alpine type veins occurring both in the peridotites and in the diallagites have been studied by the writer in Poldnevni primary deposit of demantoids. This deposit lies on Bobrovka creek, 10 km S. S. W. of Poldnevnaya village, amidst a complex of ultra-basic rocks squeezed in between quartzites in the west and schistose augitic porphyrites in the east. The following rocks have participated in the geological structure of this complex: peridotites, pyroxenites, diallagites, amphibolites and serpentinites, which owe their origin to pyroxenites and partly to peridotites.

Predominant among these are the dark-green coarse-grained pyroxenites, composed of augite and magnetite, with minute islets of diallagites and peridotites. The pyroxenites have been strongly serpentinized, especially at the contact with the quartzites, and so are the peridotites.

Demantoides are mined here from two primary deposits, one occurring in diallagites, and the other in peridotites. The diallagites are cut up by fissures into a system of parallelepipedal blocks. Along the most distinctly pronounced system of fissures, of a 315° N. W. strike and a steep 85° N. E. dip, there occur small lenticular cavities, with walls encrusted with demantoides and their accessory minerals, such as magnetite, metaxite and aragonite. In the vicinity of the fissures, the diallagites are strongly altered, serpentinized and partly leached. The demantoid grains are rounded and strongly fissured: they often contain inclusions of magnetite and metaxite. These formations bear all the principal characters of Alpine type veins. They occur in a region that had been subjected to the most violent metamorphic processes, the fissures having obviously remained open throughout the period of deposition of the minerals. The paragenesis of the vein minerals corresponds

exactly to the composition of the diallagites, the carbon dioxide* alone being of an extraneous origin.

The writer had no opportunity of personally inspecting the deposit occurring in the peridotites. From the evidence of the workmen and an examination of the museum pieces of ore it was easy to infer that the demantoids had been contained in a succession of fissures running to an increasing depth through strongly serpentinized peridotites. These fissures had the same strike as the veins occurring in the diallagites. In the peridotites, the demantoids are associated with magnetite, metaxite, aragonite and calcite.

The second of the Ural demantoid deposits ([3]) is in the N.-Taghil district, where it is known as an alluvial deposit only; the demantoid occurring in it have probably also been derived from Alpine type veins, as the mineral inclusions in the demantoid grains are identical with those of Poldnevnaya deposit.

5. As early as in 1912, Academician V. I. Vernadskij suggested that the chrome chlorites ([2]) might possibly have been formed in Alpine type veins (dry fissures), but that statement passed unnoticed, and the Ural deposits of chrome chlorites have not so far been studied from this standpoint. They are mainly to be found in fissures and cavities of chromites, which mainly occur in serpentinites. The chromite fissures contain a variety of minerals, and their genesis does not always seem to be the same. Still, the fissures in the chromites of Saranovski mine with the paragenesis: uvarovite, chromamesite**, brookite**, perovskite**, prochlorite**, rhodochrome and chromrutile, are undoubtedly Alpine type veins. They must have originated in open fissures as otherwise the beautiful emerald-green crystals of uvarovite, the rose-coloured aggregates of chromamesite, etc., would not have been preserved. The chrome spinels of the ore deposit have been strongly altered, crushed; the chemical composition of the minerals contained in the fissures corresponds to the composition of the chrome spinels of that deposit. The slight admixtures of Ti and Ca to the minerals constituting the ore form independent minerals in the fussures, such as brookite, a mineral characteristic solely of Alpine type veins, perovskite, etc. A detailed study of mineral-bearing fissures in chromites from this point of view yields much important and interesting information.

6. The veins occurring in Ural greenstone rocks do not differ substantially, either morphologically, paragenetically or as to the appearance of the crystals, from the veins of the metamorphic diorites and gabbro in the Alps ([6],[7]).

The demantoid veins of the Ural peridotites and diallagites show some likeness to the Tsermatt veins ([7]) occurring at the contact of serpentinites with limestones.

As far as the writer is aware, the depositions in chromite fissures have never before been regarded as Alpine type veins.

7. A curious example of Alpine type veins is afforded by the fissures in the pyritic ores of the Urals ([5]) containing sphalerite, chalcopyrite, probably pyrite, tennantite, quartz, barite, gypsum and calcite, i. e. all the principal chemical elements of the ores are represented by independent minerals in the fissures. Closely related to Alpine veins are also the cavities in the Kussa titanomagnetites with the following paragenesis: brown spar, clinochlore and ilmenite. Unfortunately, none of these formations have been specially studied by mineralogists. Alpine type veins would appear to occur in all metamorphic rocks, wherever folding and substantial alteration of the original mineral composition have occurred. A detailed study of vein deposition in different metamorphic rocks will therefore make it possible to identify further Alpine

* And the H_2O vapours? *Acad. V. Vernadskij.*

** Personal communication of Eng. I. A. Zimin regarding the minerals of this deposit as identified by himself.

type veins and will shed light on those processes of metamorphism that took place there.

8. Koenigsberger ([6],[7]) has thus outlined the genesis of Alpine type veins. In a zone of metamorphism, water, its vapour, carbon dioxide and, possibly, some other volatile compounds gain access into fissures of dynamic origin, leach the walls of the fissures and become mineralized at their expense; subsequently, with the lowering of temperature and pressure, perfectly-shaped crystals of various minerals are precipitated out of these gaseo-aqueous solutions. The temperature range of mineral deposition is taken to lie ([7], [12]) between 500 and 100°. To form an accurate idea of the mechanism of vein formation is at present impossible, since the solubility of silicates, etc., at high temperatures and pressures is unknown. Generally speaking, the ultimate phases of all contact-metamorphic, pegmatitic ([12]) and hydrothermal processes must involve the Alpine type of mineral formation. The ultimate phases of these processes are nearly always characterized by the presence of cavities into which aqueous solutions and gases find their way. If no further materials are added, they dissolve the previously deposited minerals, and crystals are ultimately precipitated out of this re-mineralized solution. In this sens, it is legitimate to speak of a special Alpine lateral-secretory phase of minerogenetic processes.

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STRATIGRAPHY

ON THE STRATIGRAPHY OF THE SOURCES OF KATUN RIVER IN THE ALTAI MOUNTAINS

By A. NIKONOV

(Communicated by A. A. Borissiak, Member of the Academy, 15. VII. 1937)

The materials presented in this report were collected by me during a geological expedition sent to field by the Institute of Geological Survey (Leningrad), in 1930, 1931, 1932.

On the north-east, the region under discussion embraces the massif of mount Belukha; on the south it is bounded by the South-Altaï, Tarbagataï and Sarym-Sakty ranges; in the south-west it adjoins the head of the Narym river which is a right tributary to the Irtysh, and on the north-west, the spurs of the Kholzun range, from which it is separated by the wide valley of the Zelenka river. The areas represented by the summarized stratigraphic sections given below are anything but equal in size or value. The oldest deposits which I unite under the name of K a t u n s e r i e s of lower Devonian age form almost the entire region (its upland parts), and, in the north-east, extend beyond its limits.

More recent Devonian and Carboniferous deposits form mountain chains of medium height within a small tract extending along the Bukhtarma River, in the south-west; the best section of the Middle Devonian is to be observed in the rocky banks of the Belaya River breaking through the Bolshaya (Great) Listviaga Range at some distance downstream of Beloye Village; the Carboniferous is developed as a narrow zone along the right bank of the Bukhtarma below the mouth of the Sogornaya River, and is widely distributed along its left bank, spreading far beyond the limits of the region described.

The following section shows the succession of strata in descending order and from the south to the north.

Middle Devonian

10. Conglomerate with large pebbles of limestone, marble, argillaceous shale and tuff (mouth of the Belaya river), not under . . . . . 100 m.
9. Green and grey-green argillaceous shales with large cylindrical weathering pockets (?), not under . . . . . 500 m.
8. Bedded and reef limestones and marbles with *Favosites*, single corals, crinoid segments and undeterminable fossil remains; in places traversed by barite and calcite veins, not under . . . . . 2 000 m.
7. Green argillaceous and arenaceous shale, about . . . . . 500 m.
6. Conglomerates with pebbles of green and violet shale and with cemented plant remains, not under . . . . . 100 m.
5. Violet-coloured sandstones and argillaceous shales with subordinate layers of green shales (mouth of the Pashennaya river), not under . 500 m.

Lower Devonian (Katun series)

4. Violet and crimson-red argillaceous and arenaceous shales with rare plant remains (?) and subordinate acid lavas and tuffs, about . . . 500 m.
3. Green and dark-grey sandstones and argillaceous shales with microfauna (when more strongly metamorphozed, sometimes with hematite) enclose subordinate basic lava flows (village Kamenka), not exceeding . . . . . 1 000 m.
2. Alternating violet and green shales with subordinate lavas, about . . 500 m.
1. Prevailing green and dark-grey sandstones and argillaceous shales with subordinate lava flows (Bolshaya Listviaga range), not exceeding 5 000 m.

The Middle Devonian limestones and shales lifted into nearly upright folds and subsequently eroded are overlain with a sharp angular unconformity (at angles of 30—60° S.W.) by dark grey-blue sandy and clayey limestones in which, along the left bank of the Bukhtarma River, at Sobachie Village, the following fauna was discovered in 1932.* *Syringothyris* cf. *texta* Hall., *Schizophoria resupinata* Mart., *Rhipidomella* sp., *Chonetes* sp., *Spirifer* sp., *Sp.* ex gr. *attenuatus* Sow., *Camarotaechia* sp., *Chaetetes tumidus* Phill. (?), *Productus* cf. *deruptus* Rom., *Straparollus* sp., *Fenestella* cf. *compressa* Ulrich, *F. serrotula* Ulrich, *F. aff. rudis* Ulrich, *F.* cf. *multispinosa* Ulrich, *F.* sp. ex. gr. *tenax* Ulrich, *Polypora* sp. ex gr. *halliana* Prout, *Rhombopora* sp. and *Crinoidea*.

This fauna defines the Lower Carboniferous age of the enclosing beds, being indicative rather of the top parts of the Tournaisian than of the basal parts of the Visean.

The Middle Devonian age of the underlying limestones and shales is established on the base of a fauna previously collected from them by M. Janishevsky at Sogornoye village and including: *Favosites cervicornis* Blainv. (3) and *Spirifer* ex gr. *chechiel***. The possibility is not excluded of an Upper Devonian age of the uppermost member (beds 10) of the Middle Devonian succession.

Let us examine with some more detail the problem of the age of the Katun series which, in the region described, is seen to form a large fold trending in NE. direction; the section of this series given above characterizes the southwestern limb of this fold, while traced from the Bolshaya Listviaga Range to the foot of the Katun Range the same succession of rocks of the Katun series is repeated, yet in converse order.

The north-eastern limb of the fold, showing steep and even vertical dips, is contoured a long distance in advance of the foot of mount Belukha. Beginning, approximately, with the Proyezdnaya river, the sediments, retaining about the same lithological character, show a converse succession and indicate the limb of a new fold passing on to the opposite slope of the Katun range. This is just that part of V. Obruchev's «Chuya series» which constitutes the northern slope of the Katunskie Belki range and contains no limestones. V. Obruchev believes this series to be the youngest of all the metamorphic series of the region, being, however «not younger than the lowermost members of the Lower Devonian» (4).

A first indication of the Devonian age of the deposits of the region described, was given by M. Janishevsky (3). I am referring the Katun series to the Lower Devonian. Firstly, the Katun series is older than the overlying Middle Devonian, from which it is separated by a thick conglomerate series, with cemented plant remains, and shows a different attitude. A Cambrian or Silurian age up to the Dawntonian is out of the question, since in other previously studied sections Silurian and Cambrian volcanic effusions are either absent, or, when present, bear the character of submarine ones, and since, on the whole,

* Preliminary identifications by M. Janishevsky and B. Nekhoroshev.
** Verbal information.

these sections have nothing in common with those here examined. The thickness of these deposits is too great for the Dawntonian alone; this series can thus only be referred to the Lower Devonian, a Dawntonian age of the lowermost horizons of the section (in the core of the fold) being not excluded. The only possible objection, namely, that the geological history of that part of the Altaï could have been different is at variance with the facts observed.

On the basis of these data it is possible to make the following statements:

The deposits of the Katun series present for the most part continental ones characteristic of a volcanic and lagoon topography. Vigorous tectonic movements which took place just previous to the Middle Devonian, gave rise to a mountain region at the foot of which great masses of coarse clastic materials with cemented plant remains were deposited by the sea, while in the littoral zone coral reefs developed. By these orogenic movements the cycle of Caledonian folding was closed; to this phase, which corresponds to the maximum intensity of the Caledonian cycle, belongs the formation of the granodiorite massifs of the Bolshaya Listviaga range.

The time interval between the Middle Devonian and the Lower Carboniferous is still obscure to us; a break in the deposition of marine sediments in the Upper Devonian is possible.

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PLANT PHYSIOLOGY

AN EXPERIMENT IN YAROVIZING THE EMBRYOS OF WHEAT SEEDS WITHOUT ENDOSPERM

By I. N. KONOVALOV

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In connection with the study of the qualitative changes occurring in plants during their yarovization, the problem of the localization of these changes acquires considerable interest. With the exception of Academician T. D. Lyssenko's works ([2],[3]), in which he points out that these changes occur in the growing point, there are no special investigations dealing with this problem. The study of this problem, however, acquires special significance in the light of Academician N. G. Kholodny's suggestions ([4],[5]) as to the possibility of the existence of a connection between the process of plant yarovization and the growth-promoting hormones produced in the seed endosperm. This question is, moreover, important from the methodological standpoint. As is known from published papers, some investigators, in their studies of the qualitative changes occurring in plants during their yarovization, use whole seeds, while others employ for the same purpose only the embryos free of all endosperm. Therefore, further work on the problem becomes difficult without localizing the yarovization process.

The present paper briefly sets forth the results of preliminary experiments made for the purpose of solving the above problem. The object of the work was to ascertain whether normal course of the yarovization process is possible in seed embryos stripped of their endosperm, and secondly, to determine the role of the seed endosperm in the yarovization process. This work was carried out at the Laboratory of the Physiology of Development, Institute of Plant Physiology, Academy of Sciences of the USSR.

The experimental subject in our investigations was the Ukrainka. The experiments were made in the winter and spring of 1936—1937. The yarovization of the seeds was begun on December 29, 1936, and, at its close, the seeds were planted on February 13, 1937. The experiment was carried out in the following 5 variants:

1) Yarovization and planting of whole seeds.

2) Yarovization of whole seeds and planting of the embryos stripped of their endosperm, the latter being removed after yarovization and before planting.

3) Yarovization and planting of seeds stripped of their endosperm.

4) Planting of whole unyarovized seeds.

5) Planting of the embryos of unyarovized seeds stripped of their endosperm.

In order to separate the embryo from the seed endosperm, this last was soaked to 50% moisture of its dry weight and then left for 3 hours in such a state. The embryo was then stripped of the endosperm with the help of a razor. The yarovization of embryos thus prepared was conducted under conditions of non-sterile cultures on a 3% sugar solution. Inasmuch as under conditions of non-sterile cultures, the stripped embryos were easily infected by microorganisms, the sugar solution was changed every two days. The yarovization was carried out in a dark thermostat at $+2° - +3°C$ during 46 days. The embryos infected during yarovization were eliminated by simple sorting. After yarovization, the seed embryos were planted in earthenware pots and grown under hot house conditions. Each test was repeated five times. Owing to sharp changes in the conditions of growth, our plants suffered very

The Development of Plants Grown from Wheat Seeds, Embryos Yarovized on Removing Their Endosperm. Pot 5—Plants Grown from Whole Unyarovized Seeds; Pot 6—Plants Grown from Seeds Yarovized on Removing Their Endosperm; Pot 8—Plant Grown from Whole Yarovized Seeds.

much during their first days in the hot house, a considerable part of them perishing. We were therefore obliged to cultivate part of the embryos for a few days in an aqueous culture under daylight conditions before transferring them to the soil and growing them under hot house conditions. Owing to this precaution, we succeeded in growing 8 per cent of the total number of embryos subjected to yarovization. Of course, in order to combat microorganisms, we had better make use of sterile conditions of culture, as had been done by E. D. Buslova (1) but we wished to carry out our experiments under conditions as nearly resembling those applied in agricultural practice as possible. This was the reason why we did not resort to sterile culture.

The results obtained were as follows. In the variant where whole seeds were yarovized, earing commenced on April 27. The unyarovized plants, both in the variant with whole seeds and in that with embryos stripped of their endosperm, developed no ears. In the plants of the second group, i. e. in the variants

with embryos of normally yarovized seeds (the endosperm, as has been mentioned above, was removed before sowing and after yarovization), earing began on May 2. As shown by the above data, the earing of plants grown both from whole yarovized seeds and from the embryos of such yarovized seeds occurs almost simultaneously. A certain lag in development of the plants grown from embryos stripped of the endosperm is due to their slower growth during the initial stages of vegetation. When yarovization has been completed the endosperm plays no part in the development of the plant and merely supplies the embryo with nutritive substances.

The plants grown from yarovized embryos stripped of the endosperm prior to yarovization also showed normal development. The plants of this group began to ear on May 12. The later date of earing, as compared with that of the two preceding variants, may be easily explained by the slow growth of the plants of this group during the initial stage of vegetation.

The development of the plants of this group is illustrated in the figure.

We have already noted above that the endosperm does not affect the development of the embryo and the plant after yarovization; now we can add, on the basis of the data presented by the above figure, that yarovization can proceed in the seed embryos without any participation of the endosperm. The endosperm, as mentioned above, is merely a reservoir of nutritive substances for embryo. The yarovization stage may be passed by plants without the help of the endosperm if the embryo be fed artificially.

Academician N. G. Kholodny's ([4],[5]) suggestions to the effect that yarovization processes are associated with the growth hormones produced by the endosperm have not been supported by the data of our experiments. If growth hormones were associated with yarovization, they would be present in sufficient quantity in the embryo itself, and this would account for the fact that the plants in the experiments with seed embryos yarovized on removing their endosperm, bore fruit. Thus the results of our investigations justify us in drawing the following conclusions:

1. The qualitative changes occurring in seeds during yarovization are localized in their embryos.

2. Yarovization may be accomplished without the participation of the endosperm. The role of the endosperm is restricted to supplying the embryo with nutritive substances.

3. In studying the biological changes occurring during the yarovization of seeds, it is preferable to use embryos stripped of their endosperm.

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